MICROSTRUCTURES OF FELDSPATHIC GLASS IN ALH 84001 AND EVIDENCE FOR POST CARBONATE FORMATION SHOCK MELTING

Adrian J. Brearley, Institute of Meteoritics, Department of Earth and Planetary Sciences, University of New Mexico, Albuquerque, NM 87131, USA; e-mail: brearley@unm.edu

Introduction: The proposal by McKay et al. [1] that martian orthopyroxenite ALH 84001 contains evidence for fossil life has generated considerable controversy. One particular problem which is currently undergoing vigorous debate concerns the origin of the Mg-Fe-Ca-Mn carbonates which are dispersed throughout ALH 84001. A low temperature origin for these carbonates is a central tenet for the hypothesis that bacterial life existed in ALH 84001 because the putative fossil bacterial structures are found on the surface of carbonate globules. However, based on disparate results from several different studies [1-8] it is apparent that the temperature at which the carbonates formed or whether fluids were involved is highly equivocal.

In this study I have used SEM and TEM techniques to examine the relationships between carbonate and associated plagioclase-rich glass in an attempt to gain further insights into the origins of both phases. I have concentrated my studies on carbonates within crushed zones and pockets within orthopyroxene. These studies provide some new insights into the formation and shock histories of carbonate and glass in ALH 84001 and on the microstructural characteristics of the plagi oclase-rich glass itself.

The association of carbonates with feldspathic glass has been noted by several authors [3,4,8-11]. [8] argued that the coexistence of these two phases is due to the crystallization of immiscible carbonate and silicate melts, produced by shock. Alternatively, Treiman [4] proposed that the carbonate formed by the replacement of plagioclase, but it has been argued that the spherical shapes of the carbonate globules reflect replacement of an isotropic phase, i.e. glass [10]. This would suggest that formation of the feldspathic glass occurred prior to carbonate formation. [4], however, recognized that ALH 84001 has suffered two shock events and argued that the glass formed after carbonate formation. During this later shock only minor fracturing of the carbonate stratigraphy occurred. However, the relationships between carbonate and plagioclase-rich glass indicate a much more complex relationship. For example [9] has observed that carbonate fragments, clearly displaced from large carbonate globules, often occur within the glass. This observation provides very strong evidence that if the carbonate did form by replacement of feldspathic glass, a further shock event has resulted in melting of the glass and remobilization of the melt. During this process, disruption of the carbonate globules presumably occurred by injection of shock melt along fractures. Additional observations lend further support to these arguments and show that melting must have occurred in the se cond shock event.

Results: SEM studies of carbonate along crushed zones have revealed complexities in the relationship between carbonate and glass. In several areas we have observed small carbonate masses (< 100 μm) which are highly disrupted, such that they now consist of a mosaic of irregular fragments of carbonate embedded within the glass. The areas of glass which have invaded the carbonate have a very characteristic and unusual shape. Rather than penetrating along cleavage planes or fractures the glass occurs as subrounded domains, often interlinked. BSE images show that the pockets of glass show a clear zonation with a narrow layer with lower Z contrast a few microns wide adjacent to the carbonate. The presence of this zonation, the embayed character of the glass-carbonate interface and the highly corroded texture of the carbonate all provide strong evidence that the carbonate must be being replaced or resorbed by a feldspathic melt. Some extreme examples of this replacement have also been observed where separate, subrounded to irregular pockets of feldspathic glass have almost coalesced, but are separated by thin veins of relic carbonate just a few microns in width.

Fragments of carbonate which are embedded within feldspathic glass have been examined by TEM to look for evidence of interaction between the two phases which might have resulted from melting. On some interfaces between carbonate and glass a well-defined layer, 50-100 nm wide, is present. This zone appears to be a mixture of very fine-grained and amorphous material and is distinct from the glass phase adjacent to it. Analytical electron microscopy of this zone suggests that it is a mixture of feldspathic glass and carbonate, with significant concentrations of Si, Al, Na, Ca, Fe and Mg. This phase is unusually enriched in Na, with up to 20 wt% Na_2O. The glass immediately adjacent to this Na-rich phase is highly siliceous with 80-85 wt% SiO_2 and 7-11 wt% Al_2O_3. This siliceous zone extends for at least several hundred nanometers away from the carbonate grain. The interpretation of these observations is not yet clear, but silica has been observed previously in ALH 84001 [8]. It is possible that the grain boundaries between carbonate and glass were sinks for the recondensation of Na_2O lost by volatilization during shock melting [e.g. 8].

There has been considerable discussion in the literature regarding the non-stoichiometric character of the plagioclase-rich glasses, which are compositionally variable in character [3,4]. SEM and TEM observations have shed some further light on this question. High contrast BSE studies of several areas of feldspathic glass show that it has a rather heterogeneous microstructure on the 5-20 μm scale, with a texture than can be described as granular in character. This texture re-

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sults from the presence of rounded to subrounded domains of glass which are separated by very thin (<1 μm) layers or veins with lower Z contrast. The domains vary in size from several tens of microns down to < 5 μm. The veins may also penetrate into the domains of glass, but are truncated within them. In some cases, especially in large pockets of glass, this structure is better developed in the central part of the pocket. X-ray mapping of regions of glass suggest that the thin veins or layers are depleted in Na and Al and perhaps are enriched in SiO_2. TEM studies of the glass have revealed the exact nature of this compositional heterogeneity. The veins are 100-300 nm in width and can sometimes terminate at larger pockets, up to ~ 1 μm in size, within the feldspathic glass. Several veins studied consist wholly or partially of a crystalline phase, which is extremely beam sensitive and damages within seconds to a highly porous, amorphous phase. This phase is extremely rich in SiO_2 (>90 wt%), but often also contains significant Al_2O_3 (~5 wt%). As yet electron diffraction data have not been obtained from this phase, but it is clear that it has a complex microstructure which appears to be due to the presence of fine-scale twinning. It seems highly probable that this phase is a polymorph of SiO_2, possibly the high pressure polymorph, stishovite, in view of its high beam sensitivity. Further studies are required to confirm this. The presence of silica-rich zones within the glass suggests that the precursor phase was probably not stoichiometric feldspar. One possible explanation is that alteration of the glass by fluids prior to shock has caused local compositional variations. Partial replacement of the glass or plagioclase by silica, such as occurred around fumaroles at Katmai, Alaska [11] is at least one possibility. However, evidence for such alteration has been erased or modified by shock melting.

Additional evidence for the activity of fluids in ALH 84001 comes from carbonates in pyroxenes. A thin vein of carbonate, ~ 5 μm in width, has been found which extends for several hundred microns through an orthopyroxene crystal and surrounding crushed material. This vein appears to be a part of a continuous network of interconnected veins and patches of carbonate which are interstitial to broken grains of orthopyroxene. On either side of the vein, small pockets of carbonate are present up to 60 μm from the main vein. Close to the vein some pockets are connected by thin necks of carbonate to the vein itself. Although at least parts of the peripheries of the carbonate pockets are irregular in shape, many of them have interfaces with the pyroxene which are planar and clearly crystallographically controlled. Based on optical studies alone these faces appear to be parallel to the (110) cleavage of the pyroxene, although this observation needs to be confirmed by electron diffraction. As a consequence of this crystallographic control several of the pockets have shapes which are elongated parallel to the cleavage. There is strong evidence to suggest that all these pockets are interconnected in three dimensions. It has previously been noted by [4] that carbonates within crushed zones show an overall zoning which is significantly more extensive than individual grains. This phenomenon is also observed in the carbonate pockets adjacent to the vein. The pockets furthest from the vein are Mg-rich and become increasingly more Fe rich toward the vein. However, even within individual pockets, which may be no more than 10 μm in length, complex zoning can be present.

According to the model of [8] such carbonate veins should have formed by injection of a carbonate melt into the pyroxene. However, there appear to be problems with such a model. Although melt could feasibly be injected along fractures in orthopyroxene, the formation of pockets requires that void space was present within the orthopyroxene or that the carbonate melt actually dissolved the pyroxene as it was introduced. The dissolution of pyroxene by maskelynite would obviously leave some kind of compositional or mineralogical signature which is not observed. In any case it is unlikely that such a process would be effective in such a short period of time. Examination of orthopyroxene away from the vein shows that the abundance of carbonate-filled pockets decreases rapidly with distance from the vein and within 100 μm have disappeared completely. This evidence shows that the development of the pockets is closely associated with formation of the vein and indicates that that dissolution of the pyroxene must have occurred during or prior to the formation of the veins. It seems probable that some type of fluid phase was involved in this process.

Conclusions These observations show that: a) the feldspathic glass was melted and remobilized after formation of the carbonate. The carbonate globules, at least locally, were invaded and disrupted by this process and in some cases may have been resorbed by the melt. b) the heterogeneous character of the glass demonstrates that the precursor was not stoichiometric feldspar. This non-stoichiometry may have been caused by some type of alteration involving a fluid. c) Pockets of carbonate within orthopyroxene adjacent to carbonate veins suggest that they were voids, probably produced by the dissolution of pyroxene by a fluid.

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